

# **Market Assessment and Technical Feasibility Study of PFBC Ash Use**

## **Topical Report**

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## ABSTRACT

The commercial introduction of pressurized fluidized bed combustion (PFBC) has spurred evaluation of ash management options for this technology. The unique operating characteristics of PFBC compared to atmospheric fluidized bed combustion (AFBC) units indicate that PFBC ash will exhibit unique chemical and physical characteristics, and hence, unique ash use opportunities.

Western Research Institute (wRI), under sponsorship of the Electric Power Research Institute (EPRI), Ahlstrom Pyropower, Inc., and the U.S. Department of Energy (DOE) Morgantown Energy Technology Center (METC), has initiated a study of the use properties of PFBC ashes involving both an assessment of the potential markets, as well as a technical feasibility study of specific use options. The market assessment is designed to address six applications, including: (1) structural fill, (2) road base construction, (3) supplementary cementing materials in portland cement (4) bricks and blocks, (5) synthetic aggregate, and (6) agricultural/soil amendment applications.

Ashes from the Ahlstrom circulating PFBC pilot facility in Karhula, Finland, combusting western U.S. low-sulfur subbituminous coal with limestone sorbent, were made available for the technical feasibility study. The technical feasibility study examined the use of PFBC ash in construction-related applications, including its use as a supplemental cementing material in concrete, fills and embankments, soil stabilization, and synthetic aggregate production. In addition, testing was conducted to determine the technical feasibility of PFBC ash as a soil amendment for agricultural and reclamation applications.

PFBC ash does not meet the ASTM chemical requirements as a pozzolan for cement replacement. However, it does appear that potential may exist for its use in cement production as a pozzolan and/or set retardant.

PFBC ash shows relatively high strength development, low expansion and low permeability properties that make its use in fills and embankments promising.

Testing has also indicated that PFBC ash, when mixed with low amounts of hydrated lime, develops high strengths, suitable for soil stabilization applications and produces a synthetic aggregate capable of meeting ASTM/AASHTO specifications for many construction applications.

The residual calcium carbonate and calcium sulfate in the PFBC ash have been shown to be of value in making PFBC ash a suitable soil amendment for acidic soils. Additional testing is planned, and field demonstrations are to be conducted dependent upon the results of this testing.

## ACKNOWLEDGMENTS

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## EXECUTIVE SUMMARY

The commercial introduction of pressurized fluidized bed combustion (PFBC) has spurred evaluation of ash management options for this technology. The unique operating characteristics of PFBC compared to atmospheric fluidized bed combustion (AFBC) units indicate that PFBC ash will exhibit unique chemical and physical characteristics, and hence, unique ash use opportunities.

Western Research Institute (wRI), under sponsorship of the Electric Power Research Institute (EPRI), Ahlstrom Pyropower, Inc., and the U.S. Department of Energy (DOE) Morgantown Energy Technology Center (METC), has initiated a study of the use properties of PFBC ashes involving both an assessment of the potential markets, as well as a technical feasibility study of specific use options. The market assessment is designed to address six applications, including: (1) structural fill, (2) road base construction, (3) supplementary cementing materials in portland cement, (4) bricks and blocks, (5) synthetic aggregate, and (6) agricultural/soil amendment applications.

Ashes from the Ahlstrom circulating PFBC pilot facility in Karhula, Finland, combusting western U.S. low-sulfur subbituminous coal with limestone sorbent, were made available for the technical feasibility study. The technical feasibility study examined the use of PFBC ash in construction-related applications, including its use as a supplemental cementing material in concrete, fills and embankments, soil stabilization, and synthetic aggregate production. In addition, testing was conducted to determine the technical feasibility of PFBC ash as a soil amendment for agricultural and reclamation applications.

PFBC ash does not meet the ASTM chemical requirements as a pozzolan for cement replacement. However, it does appear that potential may exist for its use in cement production as a pozzolan and/or set retardant.

PFBC ash shows relatively high strength development, low expansion and low permeability properties that make its use in fills and embankments promising.

Testing has also indicated that PFBC ash, when mixed with low amounts of hydrated lime, develops high strengths suitable for soil stabilization applications and

produces a synthetic aggregate capable of meeting ASTM/AASHTO specifications for many construction applications.

The residual calcium carbonate and calcium sulfate in the PFBC ash have been shown to be of value in making PFBC ash a suitable soil amendment for acidic soils. Additional testing is planned and field demonstrations are to be conducted dependent upon the results of this testing.

## INTRODUCTION

The utilization of ash from fluidized bed combustion (FBC) units is a promising ash management option. The chemical characteristics of PFBC ash compared to other FBC ashes have generated interest in the use of the PFBC ash for various construction and agricultural applications. However, before commercial entities are ready to commit to the concept of using PFBC ash, its performance in these applications must be documented.

Western Research Institute (WRI), has completed the first year of a three-year project under sponsorship of the Electric Power Research Institute (EPRI), Ahlstrom Pyropower, Inc., and the U.S. Department of Energy (DOE) Morgantown Energy Technology Center (METC) that addresses ash use markets and options for PFBC technologies. The overall objectives of this study are to determine the market potential and the technical feasibility of using PFBC ash in high-volume use applications. The information is of direct use to the utility industry in assessing the economics of PFBC power generation, particularly in light of ash disposal avoidance achieved through marketing. Additional benefits can be realized to a utility through CO<sub>2</sub> offset credits resulting from ash penetration into certain markets that generate high levels of greenhouse gases during manufacturing (e.g., cement production).

In addition, the research and testing is resulting in the generation of generic technical feasibility data on the PFBC ash uses that could lead to novel processing options and procedures. The specific objectives of the research and demonstration effort are:

- to define present and future market potential of PFBC ash for a range of applications;
- to assess the technical feasibility of PFBC ash use in construction, civil engineering and agricultural applications; and
- to demonstrate the most promising of the market and ash use options in full-scale field demonstrations.

This report addresses the general PFBC ash markets and specifically focuses on the technical feasibility of ash use options for PFBC units using low-sulfur coal and limestone sorbent.

## MARKET POTENTIAL FOR PFBC ASH

Conventional power plant ash and FBC residue have been evaluated and used as engineering and construction materials for over a decade. A summary of FBC ash use in construction applications was provided by Bland (1994), The building construction, road and highway construction, coal mining and reclamation, agriculture and, recently, environmental restoration industries have all been markets for these coal combustion by-products. These industries consume enormous quantities of raw materials, and power plant ash has found acceptance in each of these industries.

The building industry has used fly ash as a raw material in cement production and cement replacement in concrete and concrete products, such as masonry units. Production of lightweight aggregate for concrete and concrete products has also been commercially practiced. Recently, FBC ash and flue-gas desulfurization (FGD) sludge have also been used in the building materials industry in such applications as wallboard production.

The construction industry has used power plant ashes in a number of applications, including road and highway construction, airport runways, and dams and other earthen and concrete structures. Road construction has traditionally involved ash in a number of techniques and materials, such as roller compacted concrete(RCC), soil stabilization, stabilized road subbases and bases, embankments and fills, engineered material for structural fills, synthetic construction aggregate production for concrete, asphalt paving, and road base construction.

The mining industry has used power plant ash for a number of years as a reclamation and soil/spoil amendment, for subsidence control in underground mines, for haul road stabilization, and for embankments and fills.

The agriculture industry is becoming a market for power plant ashes, AFBC ash, in particular, is finding acceptance in a number of states in agricultural applications. In this industry, the ash is used as a lime and sulfate source, micro- and macro-nutrient source, soil texture modifier, and moisture barrier for root growth. .

Each of these market industries also has the potential to consume large volumes of PFBC ash. An example of the market magnitude and potential of ash use can be seen in road and highway construction materials use statistics (Table 1).

**Table 1. Raw Materials Use in Road and Highway Construction Industry\***

Materials Consumed	Potential Replacement by PFBC Ash	Road Base and Subbases (million tons)	Asphalt Paving (million tons)	Concrete Paving, Bridges, etc. (million tons)
Aggregate	Synthetic Aggregate from PFBC Ash	<b>200</b>	215	200-240 Crushed Stone, Sand and Gravel
Crushed Stone, Sand and Gravel		<b>150</b>	100 to 125	
Total		<b>350</b>	315 to 340	
Cement	Cement/Concrete and Soil Stabilization	1 (est.)		15 to 20
Lime	No Replacement	0.8	0.1	
Asphalt	No Replacement		25	
Mineral Filler	PFBC Ash as Filler		25	
Fly Ash	PFBC Fly Ash	0.5	0.1	3 to 4
Bottom Ash	PFBC Bed Ash	0.4 to 0.5		

Total Conventional Aggregate Production (1987) 68.9 million tons,

Total Conventional Ash Use (1987) 18.3 million tons.

\* Does not include earthen materials used for fills and embankments, for which 2 million tons of fly ash was used in 1987.

Source: Compiled from data presented by Baker (1990) DOE/MC/25042-2872

The road construction industry consumes a tremendous amount of raw materials, including earthen borrow, aggregates, portland cement, asphalt cement, mineral fillers, and lesser amounts of lime.

Earthen borrow is used as a fill, backfill, or embankment material. Aggregates are used as subbase or base material, as well as in concrete and asphalt paving. Mineral fillers, such as rock fines and ash, are used in asphalt paving mixtures. Lime is also used as a stripping agent in asphalt, as well as a stabilizing agent for soils and road subbases and bases. Ash use in this market has reached 4 to 5 million tons per year.

### **Ash Use as a Supplementary Cementing Material in Concrete and Cement Production**

PFBC ash appears to be technically feasible for use in the cement industry. There are essentially three applications for PFBC ash in cement, including (1) replacement of cement in portland cement concrete; (2) pozzolanic material in the production of pozzolanic cements (e.g., Type IP); and (3) set retardant interground with cement as a replacement of gypsum.

In 1987, over 6 million tons of conventional fly ash were used as a replacement for portland cement in ready-mix concrete and concrete products. This represented approximately 82% of all of the fly ash used in the United States. Approximately 42% of all ready-mix concrete used fly ash at an average of 20% replacement of the cement.

In 1992, over 80 million tons of portland cement were produced in the United States. The use of conventional fly ash in the production of pozzolanic cement is estimated at approximately 1 million tons,

In addition, approximately 3 to 5% of all portland cement employs the use of a retardant such as gypsum or anhydrite, which is interground with the clinker during the cement production process. This market represents in excess of 2.5 million tons.

PFBC ash may compete with conventional materials in each of these markets, dependent upon the type of fuel being used and the amount and nature of the sorbent required.

In addition to the portland cement market opportunities, PFBC ash can also serve as a cementing material in the production of no-cement concrete and concrete products. AFBC ash use in no-cement concrete and concrete products has been the subject of extensive development in the United States and Canada during the 1980s (Minnick, 1982; Bland et al., 1987, 1989a, b, 1991a, b; Burwell et al., 1993). This material, originally developed as a material for subsidence control in underground mines, has been modified to have engineering properties comparable to those of portland cement concrete. The AFBC no-cement concrete has been tested in field demonstrations as a road base material, including roller compacted concrete, as a ready-mix concrete, and as masonry block mix.

### **Ash Use as Structural Fill and Embankment Materials**

The application of PFBC residue as an engineered material for structural fills and embankments represents a large-scale use option. Structural fills and embankments are numerous in the road construction, mining and industrial construction industries. Structural fills and highway embankments using conventional ash materials have been well documented through EPRI-sponsored research and demonstration activities.

The application of AFBC residue for these construction applications relies on the development of a stable ash material. Georgiou, et al. (1993) investigated the potential for the structural fill of a quarry using ash from the AES Barbers Point circulating AFBC facility, Oahu, Hawaii (Georgiou et al., 1993). The study concluded that the construction of a structural fill using AFBC ash was technically feasible and that the ash produced a fill with a high degree of strength and stability.

Bigham et al. (1993) describe the use of bubbling PFBC ash in an embankment for a road in Ohio. Although the technical details are sketchy at this time, the ash appears to have performed adequately in that demonstration,

### **Ash Use for Soil Stabilization**

The use of PFBC ash and other FBC residues for stabilization of soils has been proposed as a potentially large ash use market. This ash use application is similar to the cement stabilization of soils commonly applied in the construction industry. Soil stabilization is based on the treatment of clay soils with a material to provide strength and stability. Cement, fly ash and lime-ash materials are commonly employed at levels of 10 to 20% of the soil. FBC ashes exhibit self-cementing characteristics and, as such, have been proposed as a viable stabilizing agent. Unfortunately, certain FBC ashes with high sulfate contents may result in swelling and heaving of the soils. The use of low-sulfate PFBC residue or the use of PFBC ash in low concentrations with the soil appears to show promise, although caution is warranted.

The largest stabilization market is related to the stabilization of subbases and bases for road and highway construction. There are essentially two forms of stabilized road bases: (1) stabilization of a base material as a soil cement application; or (2) production of a stabilized road base material in a form such as roller compacted concrete. Both of these road base materials have potential for using ash (Bland et al., 1989a, b, 1991b). RCC is also used for other applications, such as dams and parking lots (Pitman, 1986). RCC made from AFBC ash has been demonstrated as part of the Tennessee Valley Authority (TVA)/EPRI-sponsored research program (Bland et al., 1989a, b, 1991b; Hunsacker et al., 1987). AFBC residue from the TVA 20MW FBC facility in Paducah, Kentucky, was used in a demonstration of RCC in McCracken County (Bland et al., 1989a, b; Hunsacker et al., 1987). PFBC ash is expected to be usable in this application, particularly in combination with controlled amounts of lime or cement.

Bigham et al. (1993) have successfully demonstrated the application of PFBC residue for the stabilization of cattle lots. In this application, the PFBC residue is mixed into the soft cattle lot soils and allowed to cure. The PFBC residue removes water from the cattle lot soil and hardens. The resultant cattle lots show improved stability and reduced cattle hoof penetration into the soils.

### **Ash Use in Synthetic Aggregate Production**

The aggregate market in the United States is enormous. In 1992, approximately 1.2 billion tons of crushed stone and approximately 0.8 billion tons of sand and gravel were produced for a market valued in excess of \$8 billion. The aggregate market encompasses conventional aggregate products, such as masonry units and ready-mix concrete. Also, with crushing, aggregates can be produced for use in asphalt paving, road base construction and even RCC. Lightweight aggregate can also be used in many structural building products.

Two circulating AFBC ash pelletizing plants have been built in the United States (Bland et al., 1993; Bland, 1994). These plants have the capacity of pelletizing 500 to 800 tons/day, respectively. The pelletization of AFBC ash was selected for ease of handling and for the possible subsequent use as a synthetic aggregate. Preliminary testing of the pelletized ash as an aggregate indicates that the material meets the strength, abrasion resistance, and other engineering requirements for its use as an aggregate (Bland et al., 1993).

Pelletization offers a major market for PFBC ashes in the production of synthetic aggregate. In addition, pelletized PFBC ash can be stored during the construction "off-season".

### **Ash Use in Agricultural/Soil Amendment Applications**

PFBC ash use as a soil amendment for agricultural and reclamation activities represents a potentially large market. There are a number of benefits that result from the application of PFBC residue to agricultural soils or mine spoils. The benefits include the modification of soil pH, supply of essential plant nutrients for crop production, increasing water infiltration, soil aggregation, and modification of texture of clay soils promoting root growth. An ash use data base for these applications resulting from years of research by universities has been compiled by the U.S. Department of Agriculture (USDA).

Ash use in agriculture has been promoted based on the presence of compounds such as lime and gypsum in the ashes (Korcak, 1980; Stout et al., 1988). As such, ash materials have the potential to be both a soil amendment and a nutrient source. Greenhouse studies have determined that the AFBC residue is as effective as ag-lime in increasing soil pH when the materials are applied in equivalent free lime rates. AFBC ash materials can also be an excellent source of magnesium, when dolomite is used as a sorbent. Application rates of AFBC residue at 1 to 5 tons per acre to agricultural lands with acidic soils, soils high in heavy metals, or soils deficient in trace metals can be beneficial.

PFBC and other FBC ashes can also be used as a soil amendment and nutrient source for revegetation of disturbed lands resulting from mining (Bennett et al., 1985; Stout et al., 1982; Sidle et al., 1978). The application of FBC residue to acidic soils and strip mine spoil can reduce the mobility of heavy metals through pH adjustment. Also, beneficial micro- and macro-nutrients have been observed to move into the subsoil of infertile acidic soils and mine spoils after application of AFBC residue, thereby promoting root penetration.

PFBC ash is expected to also meet the requirements for soil amendment applications in agriculture and reclamation. Recent studies sponsored by METC have examined the use of ash from the American Electric Power(AEP) Tidd bubbling PFBC facility in a variety of greenhouse studies. The technical feasibility of FBC ash use in agricultural applications was noted. However, the potential of magnesium imbalance was also noted as a potential side effect (Stehouwer and Sutton, 1992; Bigham et al., 1993). This is specific to those units using dolomite as a sorbent.

## **Summary**

In summary, this general review has indicated that there are a number of markets into which PFBC ash, derived from both high-sulfur and low-sulfur coal-fired units, may be able to penetrate. Unfortunately, the value of the market products and the availability of competing materials has restricted transportation distances. A number of competing materials are already established in these markets and have substantial technical performance records. However, the disposal avoidance costs associated with power plants may encourage the penetration of PFBC ash into these markets, if documented technical performance of the ash in these markets can be made available. It must be demonstrated that the technical specifications for each of these

market applications can be met. This technical feasibility/performance constitutes the second component of the present study.

### TECHNICAL FEASIBILITY OF PFBC ASH USE OPTIONS

Ashes from Ahlstrom Pyropower’s Hans Ahlstrom Laboratory circulating PFBC pilot unit in Karhula, Finland, were made available for this study. The ashes represent the material from the combustion of low-sulfur Powder River Basin subbituminous coal (Black Thunder) with and without limestone sorbent. Sulfur capture of approximately 90 to 95% was achieved in the limestone sorbent tests. These tests were conducted in support of the Des Moines Energy Center (DMEC) Clean Coal project. Powder River Basin coal and Iowa Industrial Lime No. 1 were the possible fuel and sorbent materials for the DMEC-1 circulating PFBC demonstration project.

The Ahlstrom circulating PFBC pilot plant combustor is housed in an 11.8-ft (3.6-m) diameter pressure vessel. A high-pressure, high-temperature, gas cleaning unit downstream of the PCFB exhaust is installed in a separate 8.5-ft. (2.6-m) diameter pressure vessel. The maximum plant operating pressure is 16 bar (232 psia). The fuel is fed as a slurry and the sorbent is fed along with the fuel. A separate dry sorbent feed system is also installed for trimming the sulfur oxides emissions during load swings. The plant has provisions for start-up with gas and/or oil. A detailed description of the facility is provided in earlier papers (Isaksson et al., 1990; Sellakumar et al., 1993), and the design conditions are given in Table 2.

**Table 2. Typical Operating Conditions of Ahlstrom Py-reflow Circulating PFBC Pilot Plant**

Heat Input	34 MM Btu/hr (10 MW <sub>th</sub> )
Max. Fuel Feed Rate	15870 lb/hr (2 kg/s)
Max. Air Flow Rate	43650 lb/hr (5.5 kg/s)
Operating Temperature	1616° F (1153° K)
Max. Operating Pressure	232 psia (16 bar)

Two sets of fly ash and bed ash from the combustion trials at the Ahlstrom facility were used in the study. The ashes represented combustion of the low-sulfur Black Thunder coal and the limestone sorbent operated at Ca/S ratios of 0 and 2-3.

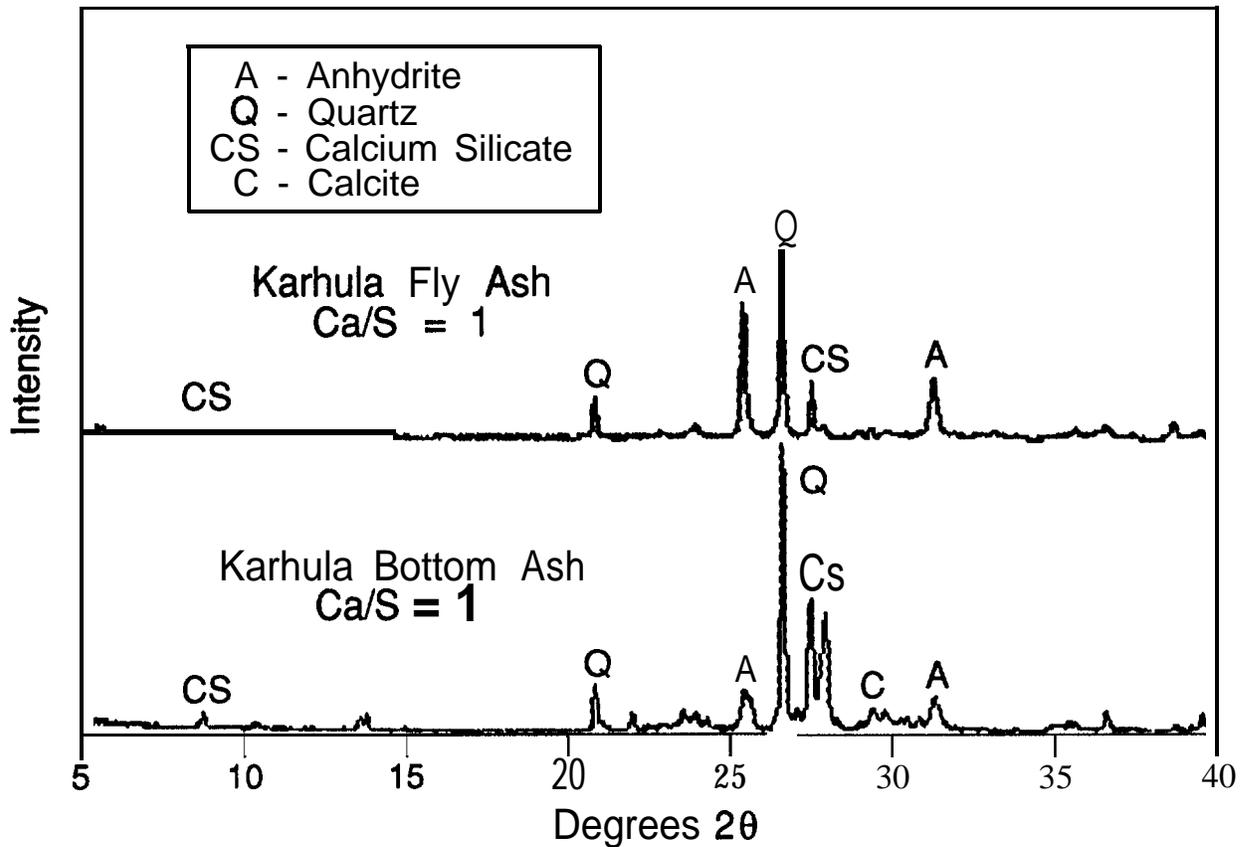
The Ca/S=0 and Ca/S=2-3 ashes were separately proportioned and combined to represent a fly ash and bed ash as operated at a Ca/S ratio of approximately 1. This was considered technically defensible, since the Ca/S=0 and Ca/S=2-3 tests were conducted under similar temperature ranges of around 800° C. The Ca/S=1 ashes were used in the testing described in this paper.

### **Ash Characterization and Conditioning Studies**

Representative ash from each of the Karhula runs was subjected to a series of chemical and physical tests, The chemical compositions of the Karhula ashes are presented in Table 3. Phase analysis of the ashes was conducted using x-ray diffraction (XRD), scanning electron microscopy (SEM) and thermo-gravimetric analysis (TGA). The XRD scan for the Ca/S= 1 fly ash and bed ash samples is presented in Figure 1.

**Table 3. Summary of the Chemical Composition of Karhula PFBC Ashes**

PFBC Ash	Karhula Fly Ash	Karhula Bed Ash	Karhula Fly Ash	Karhula Bed Ash	Karhula Fly Ash	Karhula Bed Ash
Ca/S Ratio of Test Run	0	0	1	1	2-3	2-3
Moisture (wt.%)	0.08	0.04	0.09	0.06	0.10	0.07
Total Carbon (wt.%)	0.10	0.04	0.13	0.52	0.28	1.23
LOI (wt. %)	0.14	1.30	0.81	0.84	1.81	3.24
SiO <sub>2</sub> (wt. %)	38.18	52.92	37.84	47.02	37.33	50.75
TiO <sub>2</sub> (wt. %)	0.87	0.45	0.87	0.40	0.86	0.32
Al <sub>2</sub> O <sub>3</sub> (wt. %)	14.77	14.43	14.27	14.57	14.78	11.47
Fe <sub>2</sub> O <sub>3</sub> (wt. %)	4.53	3.31	4.95	3.80	5.59	2.58
CaO (wt. %)	19.60	13.82	21.61	16.13	24.62	17.22
MgO (wt. %)	3.29	1.53	3.07	2.23	2.73	0.91
K <sub>2</sub> O (wt.%)	0.77	2.97	0.97	2.09	1.28	3.59
Na <sub>2</sub> O (wt. %)	1.53	2.93	1.55	2.37	1.59	2.25
P <sub>2</sub> O <sub>5</sub> (wt. %)	0.79	0.31	0.76	0.50	0.72	0.20
SO <sub>3</sub> (wt. %)	14.86	5.74	12.17	9.39	8.13	7.27
CO <sub>2</sub> (wt. %)	0.37	0.11	0.55	1.77	0.81	4.25
Total	99.64	98.56	99.20	100.33	98.54	100.88



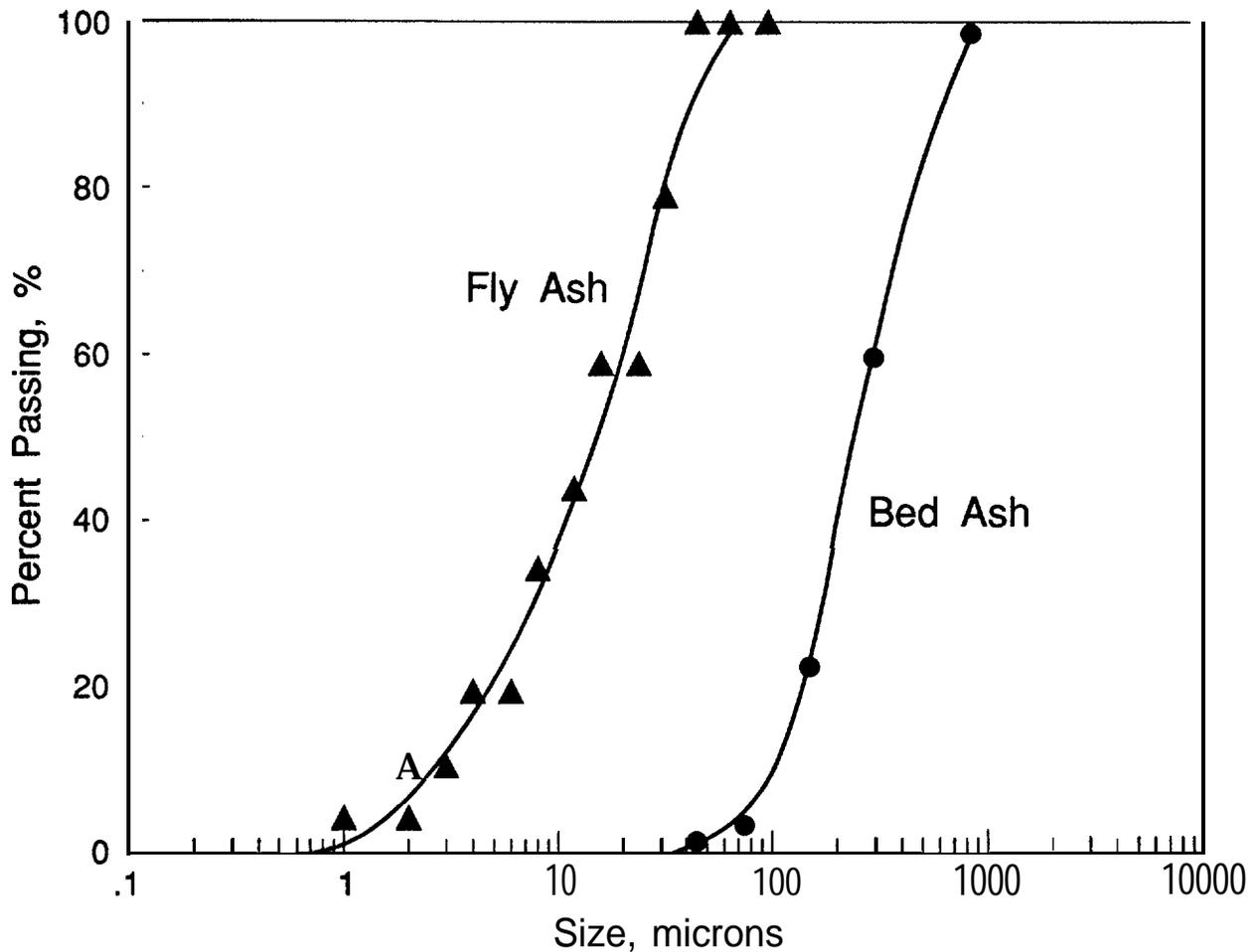
**Figure 1. X-Ray Diffraction Scan of Karhula Ca/S=1 Fly Ash and Bed Ash**

The XRD phase analysis results indicated the ashes were composed principally of anhydrite ( $\text{CaSO}_4$ ), calcite ( $\text{CaCO}_3$ ), coal ash oxides, and dehydroxylated clays. Minor amounts of lime were observed by TGA and wet chemical methods.

The lack of lime ( $\text{CaO}$ ) in the PFBC ashes is distinctly different from AFBC ashes, which contain large amounts of lime. In PFBC systems, the partial pressure of  $\text{CO}_2$  favors the equilibrium conditions of both calcination and recarbonization. This results in low lime and high carbonates (calcite or dolomite) in PFBC ash and high lime and low carbonates in the AFBC ash.

A set of peaks was noted that possibly represents calcium silicate phases. An investigation has been initiated to isolate and identify the exact composition of these calcium silicate phases, following the techniques described by Iribarne et al. (1993). This identification was intended to define the mode of occurrence of calcium silicates in the combustion system, as well as their role in the hydration process.

The general physical properties of the ashes were also determined, including particle size distribution, specific gravity, and bulk densities. The particle size distribution of the Karhula Ca/S=1 composite fly ash and bed ash materials is presented in Figure 2. The size distribution is similar to that of other FBC ashes reported in the literature (Georgiou, et al., 1993; Bland, et al., 1993b; Bigham, et al., 1993).



**Figure 2. Particle Size Distribution of the Karhula Ca/S=1 Fly Ash and Bed Ash**

The bulk densities of the Karhula Ca/S=1 composite fly ash and bed ash materials were also determined according to ASTM procedures. The bulk densities were 59.2 pcf (poured) and 72.5 pcf (packed) for the fly ash and 85.4 pcf (poured) and 95.4 pcf (packed) for the bed ash from the Karhula Ca/S=1 run. Specific gravities for the Karhula Ca/S=1 fly ash and bed ash materials were determined to be 2.8 and 2.7 g/cc, respectively.

Conditioning tests were also conducted on the bed ashes from the Karhula Ca/S=1 test ashes. As expected, there was no temperature rise, due to the lack of either lime (CaO) or periclase (MgO) in the ashes (Figure 1). Lime and periclase hydration are the main exothermic reactions that can occur during conditioning. As a result, preconditioning of the Karhula ashes was considered unnecessary.

**Feasibility Testing - Ash Use as a Supplementary Cementing Material in Concrete and Cement Production\***

PFBC ash appears to have technical feasibility for use in the portland cement industry, including: (1) replacement for cement in portland cement concrete, (2) pozzolanic material in the production of pozzolanic cements (e.g., Type 1P), and (3) set retardant interground with cement as a replacement for gypsum. Since PFBC ash appears to show promise for each of these applications, testing was initiated to examine the technical compliance of the Karhula PFBC ash.

**Cement Replacement.** The use of PFBC ash in concrete and concrete products relies on the pozzolanic property of the ash. Fly ash, including FBC ash, is known to be a pozzolan and therefore is used as a cement replacement (supplement) in portland cement concretes. The use of PFBC ash as a pozzolan for portland cement and concrete products is dependent upon a number of characteristics tested according to ASTM C-311 and specifications of ASTM C-618. The fly ash from the Karhula Ca/S=1 runs was analyzed for chemical and physical properties as related to the use of the fly ashes as a pozzolan for cement replacement in portland cement and concrete products. The results are presented in Table 4.

**Table 4. Summary of Results of ASTM C-311 Testing of Karhula Fly Ash**

	Karhula Fly Ash	ASTM C-618 Specifications	
	Ca/S=1	Class F	Class C
<b>Chemical Properties</b>			
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> (wt.%)	57.57	70 min	50 min
Sulfur Trioxide (wt.%)	12.17	5 max	5 max
Moisture Content (wt. %)	<b>0.09</b>	<b>3 max</b>	<b>3 max</b>
Loss on Ignition (wt.%)	0.81	6 max	6 max
Available Alkalis (wt.%)	<b>0.70</b>	1,5 max	<b>1.5 max</b>
<b>Physical Properties</b>			
Fineness (% retained 325 mesh)	25.58	<b>34 max</b>	34 max
Pozzolanic Activity Index -PC (% of control @ 28 d)	83.4	75 min	75 min
Water Requirement (% of control)	97.7	105 max	105 max
Soundness - Autoclave Expansion (%)	<b>-0.040</b>	<b>0.8 max</b>	0.8 max

The data indicate that the ashes do not qualify as pozzolans according to ASTM C-311 due to the sulfate levels in the ashes exceeding the ASTM C-618 specification of 5% maximum  $\text{SO}_3$  content. This will restrict the use of certain PFBC ashes as pozzolans for portland cement applications. The use of dolomite as a sorbent in PFBC can also result in high MgO contents, exceeding the 4% ASTM limit in cement.

**Portland Cement Production.** In addition, ash can be incorporated into the cement manufacturing process as an ingredient in the clinker production and secondly as an interground material in the production of Type 1 pozzolanic cements. The characteristics of the ash for these applications are defined under ASTM C-595 and 593. The use of ash as a pozzolan in a blended cement as per ASTM C-595 does not rely on the chemical properties of the pozzolan and instead sets performance specifications for the resultant blended cement. Testing related to the potential use of the PFBC ashes in the manufacturing of blended Type 1P cement has been initiated, but the results are not available at this time.

**No-Cement Concrete.** In addition to its use in portland cement and portland cement products, PFBC ash may have a possible use as a total cement replacement similar to AFBC concrete products (Burwell, et al., 1993; Bland et al, 1989a, b), when used in conjunction with lime. PFBC ash, unlike AFBC ash, does not contain sufficient free lime for developing the pozzolanic reactions responsible for strength development. Related testing is underway, but results are not available.

### **Feasibility Testing – Ash Use as Structural Fill and Embankment Materials**

The application of FBC residue as an engineered material for structural fills and embankments represents a large-scale use option. Structural fills and embankments are numerous in the road construction, mining and industrial construction industries. PFBC ash is expected to be marketable for these applications.

Geotechnical testing of the Karhula ashes was conducted as related to its possible use as a structural fill or embankment material. The geotechnical testing focused on the moisture-density relationship (Proctors), unconfined compressive strength, expansion and swell, and permeability.. A description of the results of testing for each of these properties for the ashes is provided below.

**Mo' ture-Density Relationships for the Karhula Ashes.** ASTM moisture-density relationships were determined using D-698 and D-1557 compactive efforts. The D-1557 compactive effort is twice that for D-698. The results are presented in Table 5.

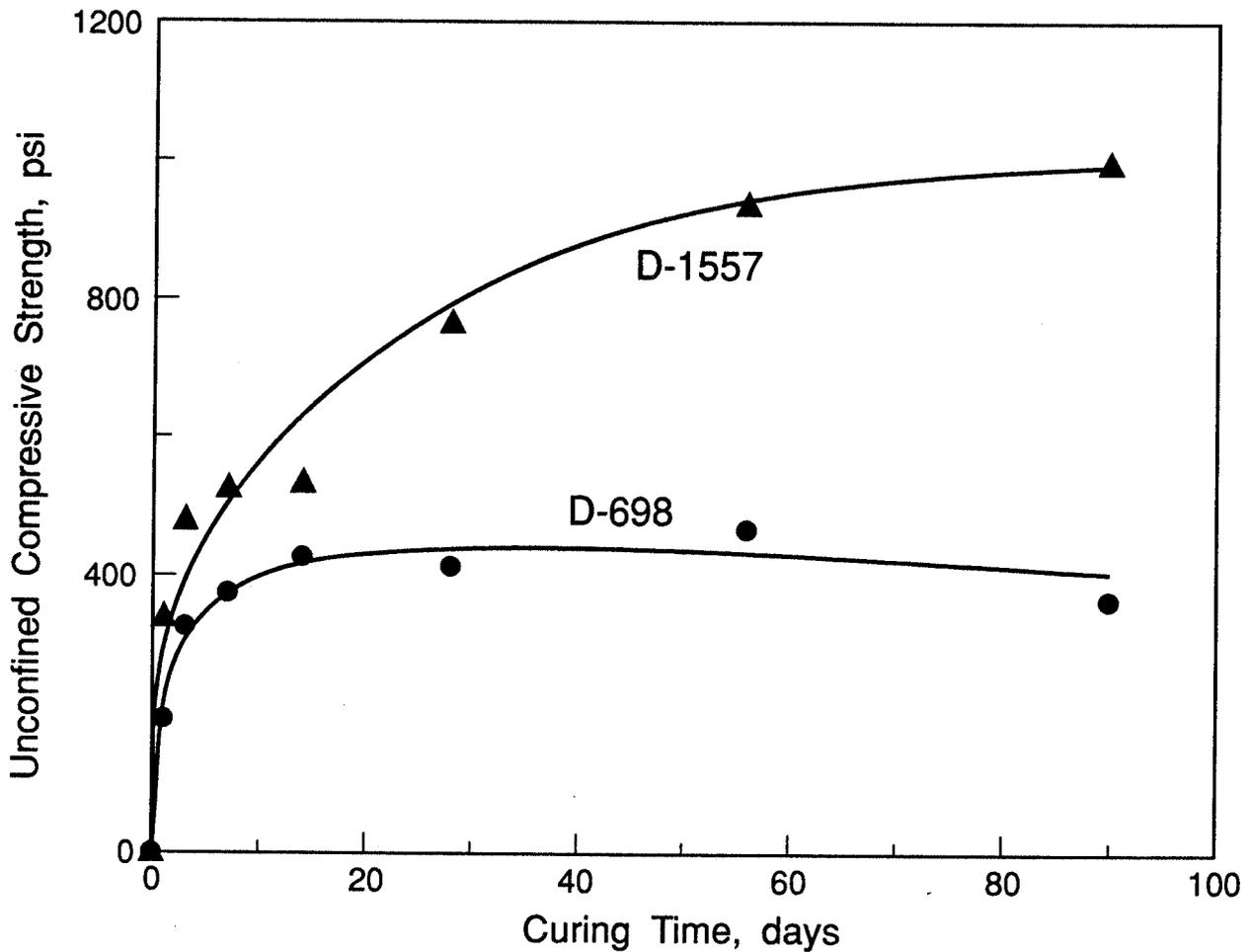
**Table 5. Moisture-Density Relationships of Karhula Ca/S=1 Ashes**

	ASTM D-698	
	“Optimum” Moisture (%)	Max. Dry Density (pcf)
Fly Ash	29.0	87.2
Ash Blend	24.8	94.0
	ASTM D-1557	
	“Optimum” Moisture (%)	Max Dry Density (pcf)
Fly Ash	26,6	92.9
Ash Blend	21.2	99.5

The “optimum” moistures and maximum dry densities are as expected. The lower “optimum” moisture and higher maximum dry density observed for the bed ash is consistent with the larger particle size and specific gravity of the bed ash relative to the fly ash. The ASTM **D-698** and D-1557 modified Proctor data are consistent with the expected behavior of different compactive efforts (i.e., lower “optimum” moisture and higher maximum dry density for increased compactive effort).

**Unconfined Compressive Strength Relationship.** Testing was conducted to address the strength development of the Karhula Ca/S=1 ash blend. The ash blend is a composite of the fly ash and the bed ash in approximate proportions to that produced in the combustion trials (80% fly ash and 20% bed ash). Testing was conducted at the optimum moisture and densities represented by the ASTM D-698 and D-1557 (Table 5). The curing was conducted under sealed (100% relative humidity) and saturated conditions at 23° C. Typical results of the testing are graphically displayed in Figure 3 for the Ca/S=1 ash blend.

Figure 3 shows strength development for the Ca/S=1 ash blend under sealed conditions for different compactive efforts. Although the strength development is low compared to that of AFBC ash, the strength development of the Karhula PFBC ash is a factor of 4 to 10 times higher than that for other soils and fill materials. As expected, the ASTM D-1557 compacted specimens show an increase in strength compared to the ASTM D-698 compacted specimens. The higher compacted material results in shorter inter-particle distances and hence allows for a greater binding efficiency of the hydration reaction products, such as ettringite and gypsum.



**Figure 3. Strength Development of Karhula Ca/S=1 Ash Blend for ASTM D-698 and D-1557 Compactive Efforts, Sealed Curing (23° C)**

**Expansion Properties.** The expansion properties of the conditioned and D-698 and D-1557 compacted Karhula ashes were determined according to modified ASTM C-157 procedures in which the expansion is essentially unrestricted, since the ashes are demolded after one day of curing. The results for the Karhula Ca/S=1 ash blend for D-698 and D-1557 compactive efforts are essentially identical, with expansion of near zero percent. In addition, the D-698 and D-1557 compacted ash blend specimens cured under sealed and saturated conditions also showed essentially no expansion. This is as expected, since there is little lime available for the reaction to form ettringite, which is considered along with gypsum to be major causes of expansion in FBC ashes. The Karhula Ca/S=1 ash blend is dimensionally stable and thereby suited for fill and embankment applications.

**Chemical Reaction Basis of Strength and Expansion Properties**, The chemical basis for the observed strength and expansion behavior of the Karhula Ca/S=1 ash blend was determined by XRD, TGA and wet chemical methods. The chemical behavior of the D-1557 and the D-698 specimens is essentially identical, showing minor development of ettringite and gypsum with curing time. As a result, the observed strength differences appear to be related to compaction and not to the chemical reaction kinetics or products.

The Karhula ashes that were cured under saturated conditions differed from those cured under sealed conditions. Under saturated curing conditions, there was a continued slow hydration of the ash resulting in the formation of gypsum from anhydrite with time. Interestingly, this long-term and slow formation of gypsum (known to be expansive) does not appear to contribute to expansion as one might have expected.

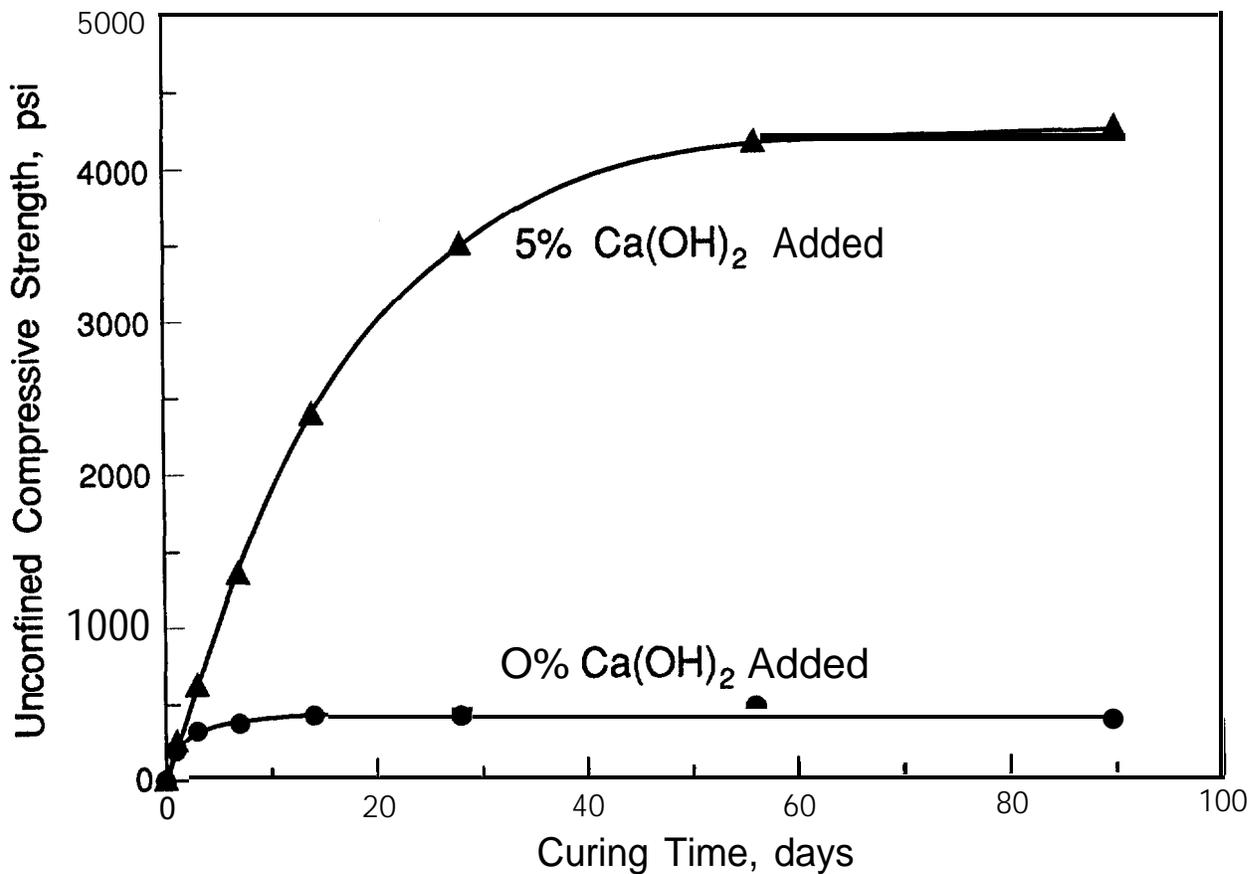
**Permeabilities**.<sup>\*\*</sup> The permeability of the Ca/S=1 Karhula ash blend was determined according to ASTM procedures. The ashes were compacted to ASTM D-698 compactive effort at “optimum” moisture. As expected, the permeability of the ash blend continued to decrease with curing. Hydraulic conductivities in the range of  $9 \times 10^{-6}$  cm/sec were determined at early ages and continued to decrease to values of  $2 \times 10^{-6}$  cm/sec, after which the values appeared to stabilize. These values are typical of those reported for CFBC ashes (Georgiou, et al., 1993).

### **Feasibility Testing - Ash Use for Soil Stabilization**

PFBC ash use for soil stabilization is similar to the cement stabilization of soils commonly applied in the construction industry. Soil stabilization is a method of treating a soil with a cementing material to increase its strength and durability characteristics.

In order for a material to be considered as a cementing agent for soil stabilization applications, the material must show strength development, freeze/thaw durability, and wet/dry durability in compliance with ASTM D-1632, D-560, and D-559, respectively. A viable cementing material needs to exhibit sufficient strength in the range of 4000 psi and durability of 12 cycles of freeze/thaw and wet/dry for the cementing material only. Requirements of the stabilized soil of 400 psi and 12 cycles of wet/dry and freeze/thaw must be met when the soils are treated at 10 to 20% cementing levels.

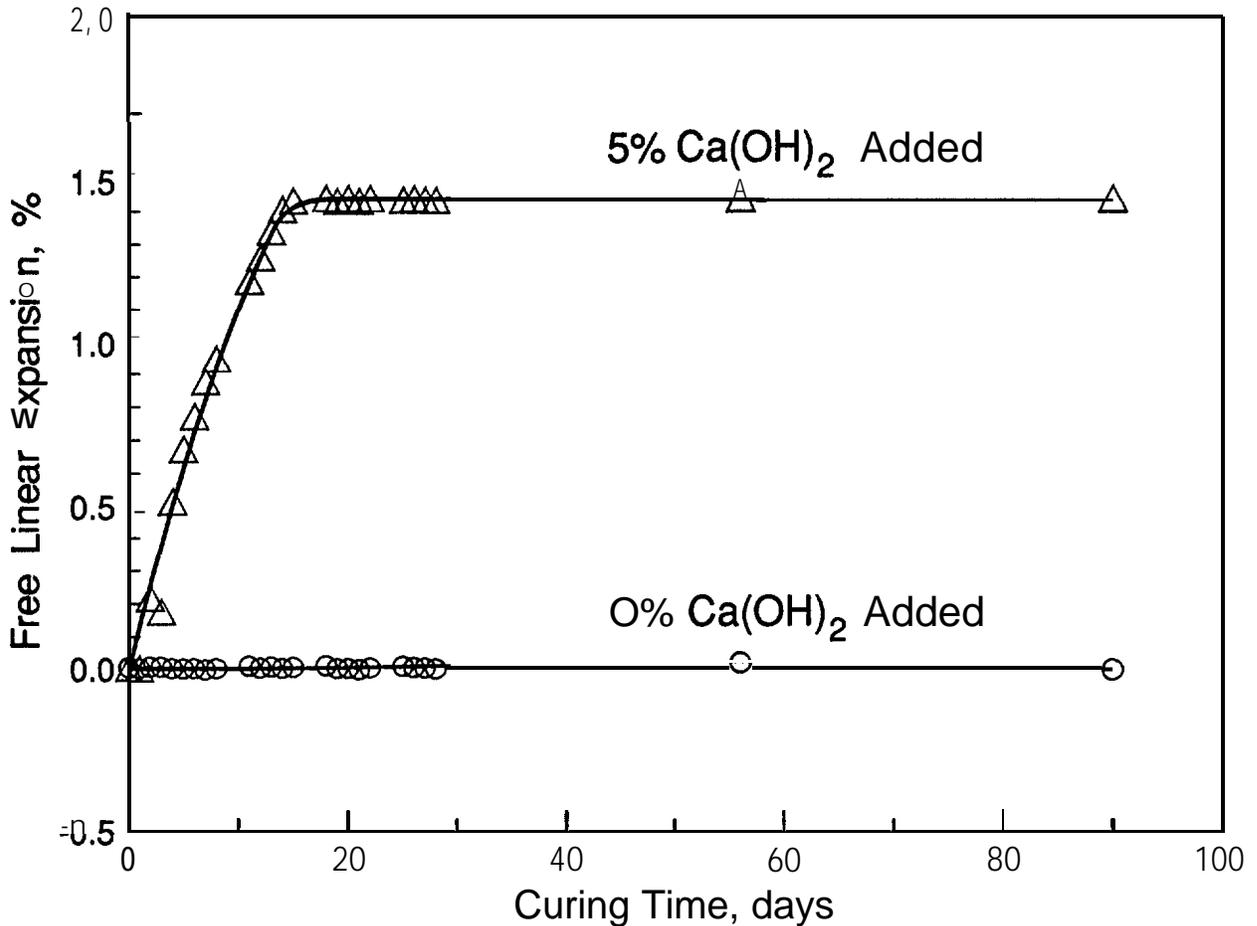
**Unconfined Compressive Strength Relationship,** Testing was conducted using the Karhula Ca/S= 1 ash blend with and without hydrated lime addition, as a cementing agent for soil stabilization applications. The test specimens were cured under sealed and saturated conditions (23° C). Typical results of the testing are graphically displayed in Figure 4 for the Ca/S=1 ash blend. The results showed 5% hydrated lime increased the strength development dramatically (over 6,000 psi at 90 days). The ash blend without hydrated lime enhancement showed strengths of less than 1000 psi. The low strengths of the ash blend without lime are sufficient for many applications, such as fills and embankments. However, for other applications, such as soil stabilization, hydrated lime enhancement will probably be required at some level (e.g., 5% or less).



**Figure 4. Strength Development of Karhula Ca/S=1 Ash Blend With and Without Hydrated Lime Enhancement, D-698 Compaction, Sealed Curing (23° C)**

**Expansion Properties.** The expansion properties of the conditioned and compacted Karhula ashes with and without hydrated lime addition were tested as

a cementing agent for soil stabilization applications, according to a modified ASTM C-157 procedure described earlier. The Karhula ashes with and without hydrated lime addition were conditioned and compacted at the ASTM D-698 “optimum” moisture and proctor density. The results are shown in Figure 5.



**Figure 5. Expansion Characteristics of Karhula Ca/S=1 Ash Blend With and Without Hydrated Lime Enhancement, D-698 Compaction, Sealed Curing (23° C)**

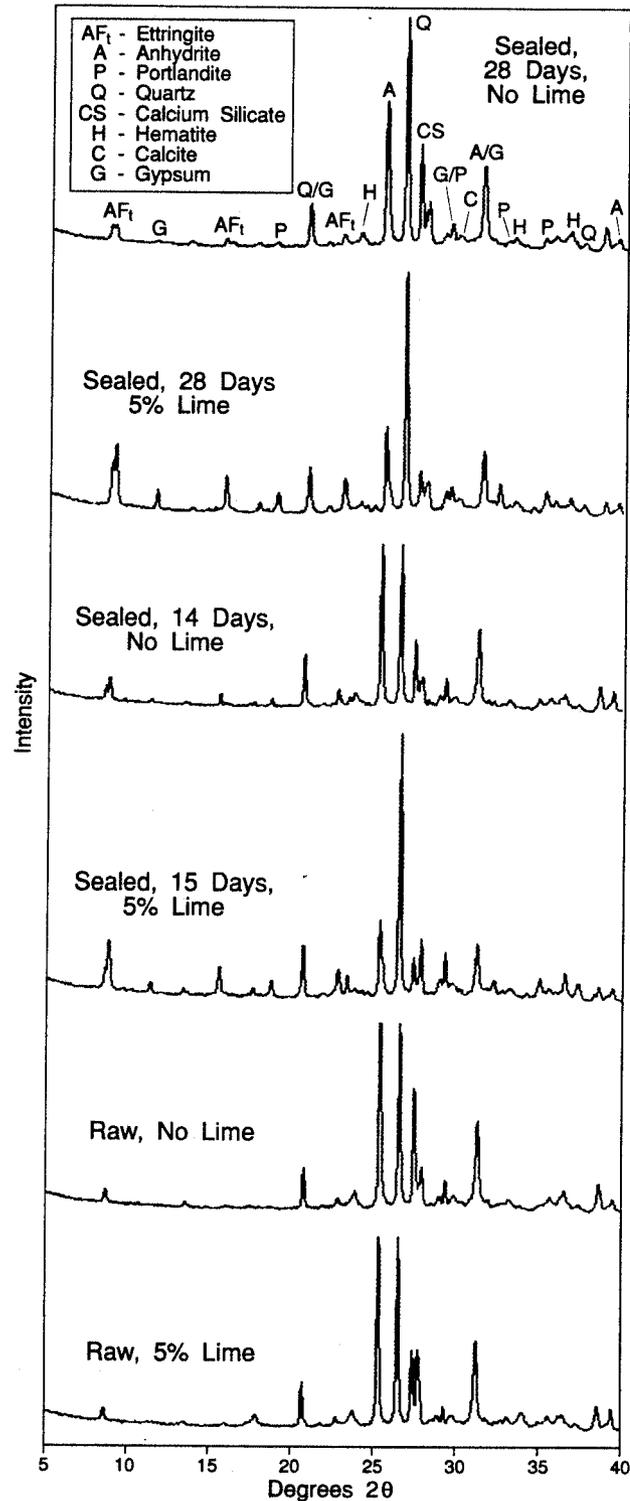
The data (Figure 5) show the expansion characteristics of the lime-enhanced Karhula ashes under varying curing conditions. The lime-enhanced Karhula ash blend (Ca/S=1) showed expansion in the range of 1.5%, while the ash blend without lime enhancement showed essentially no expansion. The expansion noted for the lime-enhanced ash appears to occur early, within the first 20 to 30 days. Although the expansion is significant, it appears controllable and manageable, and it should be possible to balance the strength and swelling properties in certain applications. For example, in certain grouting applications, controlled expansion of the magnitude reported is desirable.

**Chemical Reaction Basis of Strength and Expansion Properties.**

There is a chemical basis for the observed superior strength, expansion and durability characteristics of the lime-enhanced Karhula ashes. Figure 6 shows the comparison of XRD scans for the Karhula ash blend with and without hydrated lime addition after 14 and 28 days. The hydrated lime-enhanced Karhula ash exhibited consumption of hydrated lime and anhydrite to form ettringite, known to be both a source of strength and, along with gypsum, a cause of expansion.

**Freeze/Thaw and Wet/Dry Cycles.**

Conditioned and compacted Karhula Ca/S=1 ash blend specimens were subjected to 12 cycles of freeze/thaw (ASTM D-560) and wet/dry (ASTM D-559). The results indicated that the ashes without lime enhancement did not survive the 12 cycles, while those with 5% lime addition survived the entire 12 cycles with losses less than the 15% maximum limit. Additional testing, using a plastic and a non-plastic soil at typical stabilization rates (e.g., 10 to 20%) is being conducted.



**Figure 6. X-ray Diffraction Scans of Karhula Ca/S=1 Ash Blend With Hydrated Lime Enhancement at Various Curing Ages**

## **Feasibility Testing – Ash Use in Synthetic Aggregate Production**

As mentioned earlier, the aggregate market in the United States is enormous, Synthetic aggregate has been manufactured from power plant ash that can meet the requirements for conventional aggregate products, such as masonry units and ready-mix concrete, and with crushing can be produced for use in asphalt paving, road base construction and even RCC. As such, synthetic aggregate for construction applications appears to be a major market for PFBC ashes, as well as a method for storage of ash in the construction “off-season”.

Preliminary tests have been conducted that address the potential of pelletizing the Karhula ash to produce a synthetic aggregate material.

**Pelletizing Trials.** Pelletizing trials were conducted simulating the AET process described in the literature for the pelletization of FBC ashes (Bland et al., 1992, 1993 b). Pelletizing trials were conducted at the WRI Waste Management Laboratory, employing a high-speed pin mixer for conditioning of the ash and a 3-foot diameter pelletizing pan for the agglomeration of the conditioned ash into a pelletized form.

Two pelletizing trials have been conducted, employing Karhula Ca/S=1 ash blend with and without hydrated lime addition, The operating parameters, including water demand, are presented in Table 6.

The pelletizing trials were conducted to address the water requirement and other processing parameters pertinent to defining the technical feasibility and relative economics of aggregate production from PFBC ashes.

**Pelletized Ash Testing.** The pelletized aggregate was tested according to ASTM procedures as they relate to its use in various construction applications. Pelletized ash from each of the pelletizing trials has been tested for crush strength, Los Angeles (LA) abrasion resistance (ASTM C-131) and soundness (ASTM C-87). The results of the LA abrasion testing are presented in Table 6. The results indicate that without hydrated lime addition, the pelletized PFBC ash does not meet the ASTM or AASHTO construction aggregate requirements of a maximum of 40 to 50% weight loss, However, the addition of 5% hydrated lime results in compliance with ASTM and AASHTO requirement for construction aggregate.

**Table 6. Summary of Pelletizing Trial Conditions and Properties of PFBC Synthetic Aggregate**

<b>Ahlstrom Laboratories Karhula PFBC</b>	<b>Pelletizing Trial # 1</b>	<b>Pelletizing Trial # 2</b>
<b>Mix Components (wt. %)</b>		
Karhula Ca/S=1 Fly Ash	80.0%	76.5%
Karhula Ca/S=1 Bed Ash	20.0%	19.5%
Hydrated Lime Additive	none	4.3%
Water - Pin Mixer & Pelletizer (% of dry ash+ additives)	26.1%	20.9%
<b>Aggregate Crush Strength (lb)</b>		
24 hr	23	323
48 hr	24	306
7 days	31	340
<b>LA Abrasion Resistance</b>		
Grade	B	B
Loss at 28 days (%)	75.29	26.07

Curing Conditions -1800 F Sealed for 24 hours.

### **Feasibility Testing - Ash Use in Agricultural/Soil Amendment Applications**

This testing program is designed to provide information that will demonstrate the use of PFBC ash as a soil amendment to ameliorate acid soil problems. The potential use of PFBC ash as a soil amendment in reclamation and agricultural applications is due to the presence of nutrients, calcium carbonate (ag-lime) and gypsum. The availability of nutrients, such as sulfur, potassium, phosphorous, and the micronutrients, is expected to benefit plant growth. In addition, the neutralization potential of the ash materials can alleviate acid conditions found in many soils. PFBC ash contains anhydrite or gypsum, often used to reclaim sodic materials (i.e., materials influenced by high levels of sodium). Research to demonstrate the amelioration of sodic soil conditions has been initiated, but is not reported in this report. Both laboratory equilibrium studies and greenhouse productivity testing were conducted.

**Laboratory Equilibrium Study.** The laboratory equilibration study is designed to determine the potential of the ash materials to neutralize the available acid and the potential acid associated with oxidized and reduced materials. An acid spoil material from Texas was used for the study.

Humidity cells were used to simulate the oxidation of acid-forming soils under amended and nontreated conditions. Ag-lime ( $\text{CaCO}_3$ ) and Karhula Ca/S=1 fly ash were used as the soil neutralization amendment materials in the equilibrium humidity cell studies. The acidic materials with no neutralization amendment treatment were also used as a baseline case to determine the further oxidation and acidification of the acid soils under humidity cell conditions.

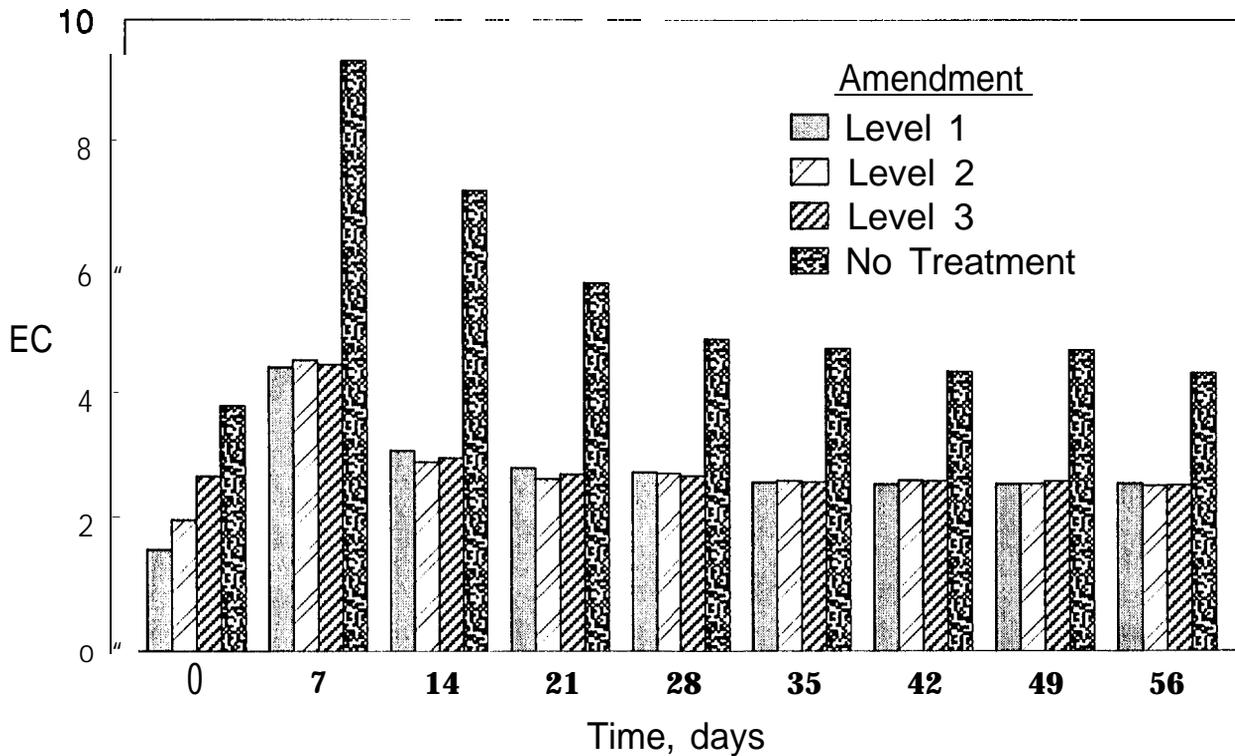
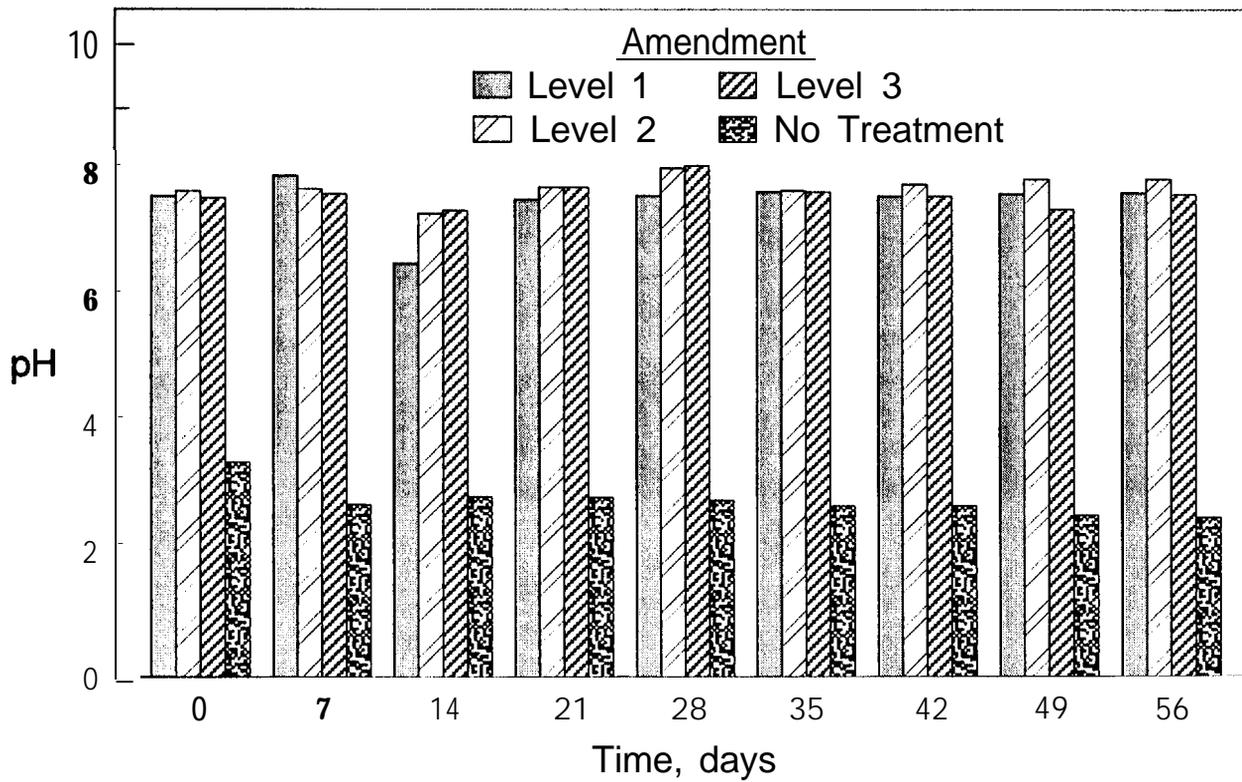
The pH and electrical conductivity (EC) results with humidity cell weathering of the untreated and the ag-lime treated acid spoil are presented in Figure 7. The acid spoil material was treated with three levels of ag-lime:

- level 1 = 30.4 g ag-lime/1000 g of spoil material
- level 2 = 26.2 g ag-lime/1000 g of spoil material
- level 3 = 17.6 g ag-lime/1000 g of spoil material

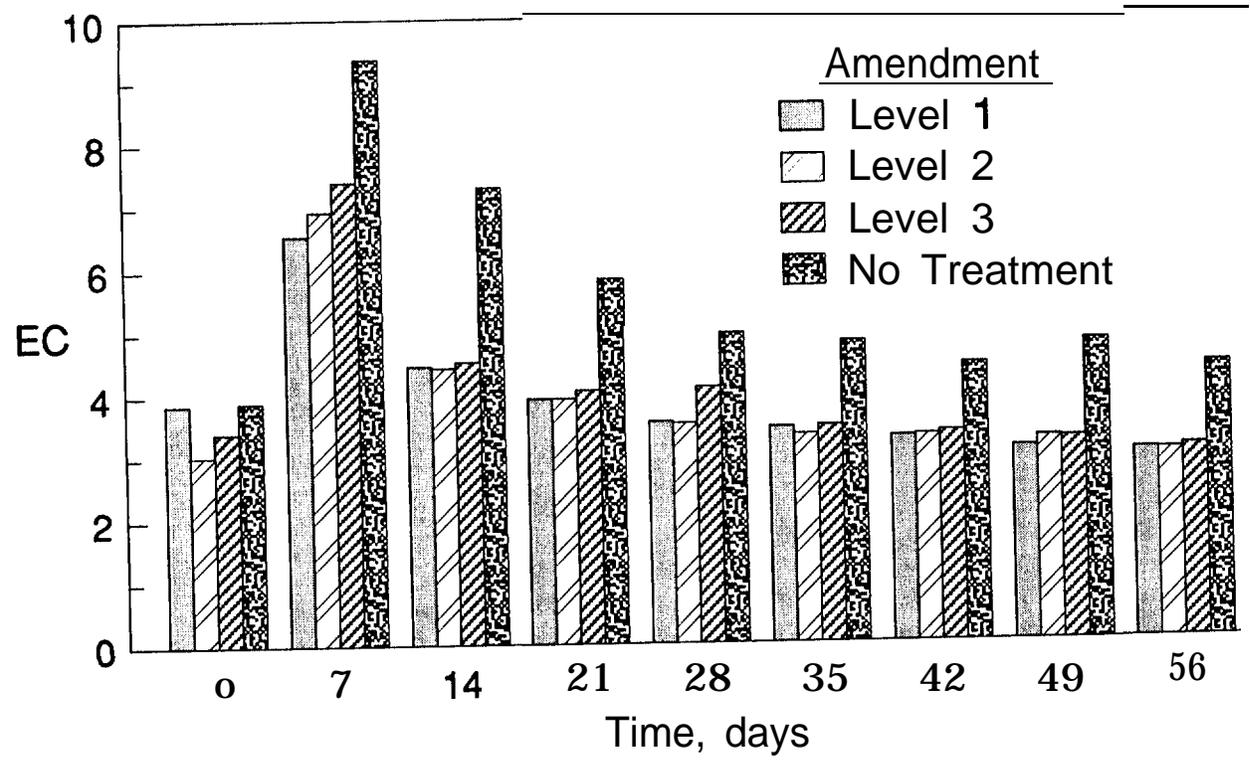
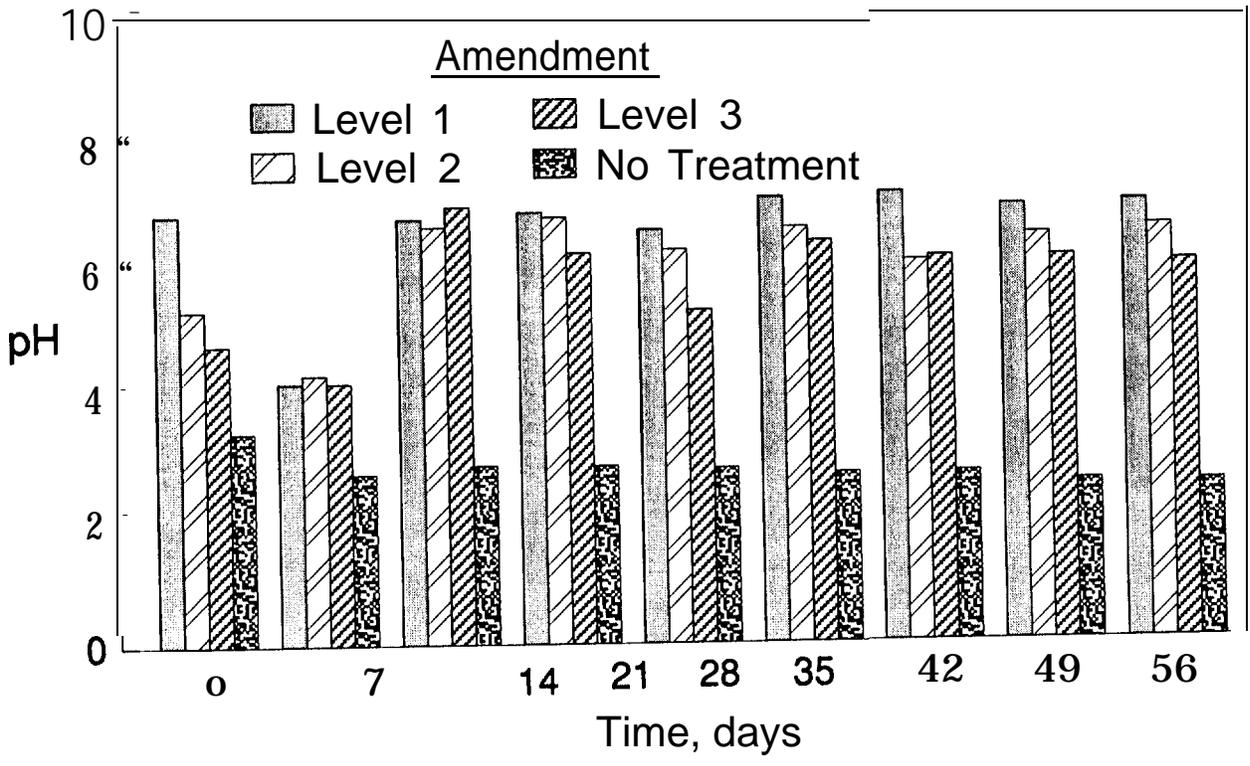
The spoils without ag-lime treatment showed continuing oxidation. The pH changes are subtle, presumably due to the buffering of the system near pH 2.7. The EC levels increased substantially early on and then decreased with time. The large increase in EC values is directly attributable to the reaction products associated with the oxidation of pyritic materials in the spoil. The acid spoil material decreased the oxidation reactions associated with pyrite and thereby reduced the amount of reaction products present in solution. The ag-lime treated spoil shows quite different pH values with time. The ag-lime reacted immediately with the spoil material, increasing the pH and maintaining it with time.

The pH and EC results with humidity cell weathering of the untreated acid spoil and the acid spoil treated with Karhula Ca/S=1 fly ash are presented in Figure 8. The amount of Karhula fly ash used was based on the calcium carbonate equivalent (CCE) of the fly ash and the acid/base accounting of the acid spoil. The Karhula fly ash application rates were equivalent to the acid neutralization potential used for the ag-lime tests. The Karhula application rates were:

- level 1 = 89.1 g Karhula fly ash/1000 g of spoil
- level 2 = 77.4 g Karhula fly ash/1000 g of spoil
- level 3 = 51.6 g Karhula fly ash/1000 g of spoil



**Figure 7. Influence of  $\text{CaCO}_3$  (Ag-Lime) on the pH and EC Values of Acidic Mine Spoil Allowed to React in Humidity Cell**



**Figure 8. Influence of Karhula Ca/S=1 Fly Ash on the pH and EC Values of Acidic Mine Spoil Allowed to React in Humidity Cell**

In general, the pH data show that the acid nature of the spoil material was neutralized by the Karhula fly ash. However, it is apparent that the reaction rate of the Karhula fly ash is slower than that of the ag-lime. The data show a pH decrease of approximately 1 unit within the first seven days. Apparently, the kinetics of acid generation of the spoil material was greater than the dissolution rate of the Karhula fly ash. After 14 days, the pH had risen to between 6 and 7, dependent upon the Karhula fly ash application rate, and remained essentially constant through 56 days in the humidity cell. Although the Karhula and ag-lime treated spoils were applied at equivalent neutralization potential, the Karhula treated spoils exhibited a 1-unit lower pH than the ag-lime treated spoils.

These types of differences can be attributed to the techniques by which the neutralization potential of fly ash materials are determined. Sometimes the acid generation reactions do not occur at the rate expected from the chemistry. Common practice, therefore, usually employs an application rate of 1.2 times that calculated from the neutralization potential determinations.

The EC data in Figure 8 for the Karhula treated acid spoil mirror the behavior noted for the ag-lime treated acid spoil shown in Figure 7. The only notable difference is the slightly higher (1 mS/cm) EC values for the Karhula ash treatments than for the equivalent  $\text{CaCO}_3$  treated spoils. The higher EC levels are associated with the dissolution of the ash materials.

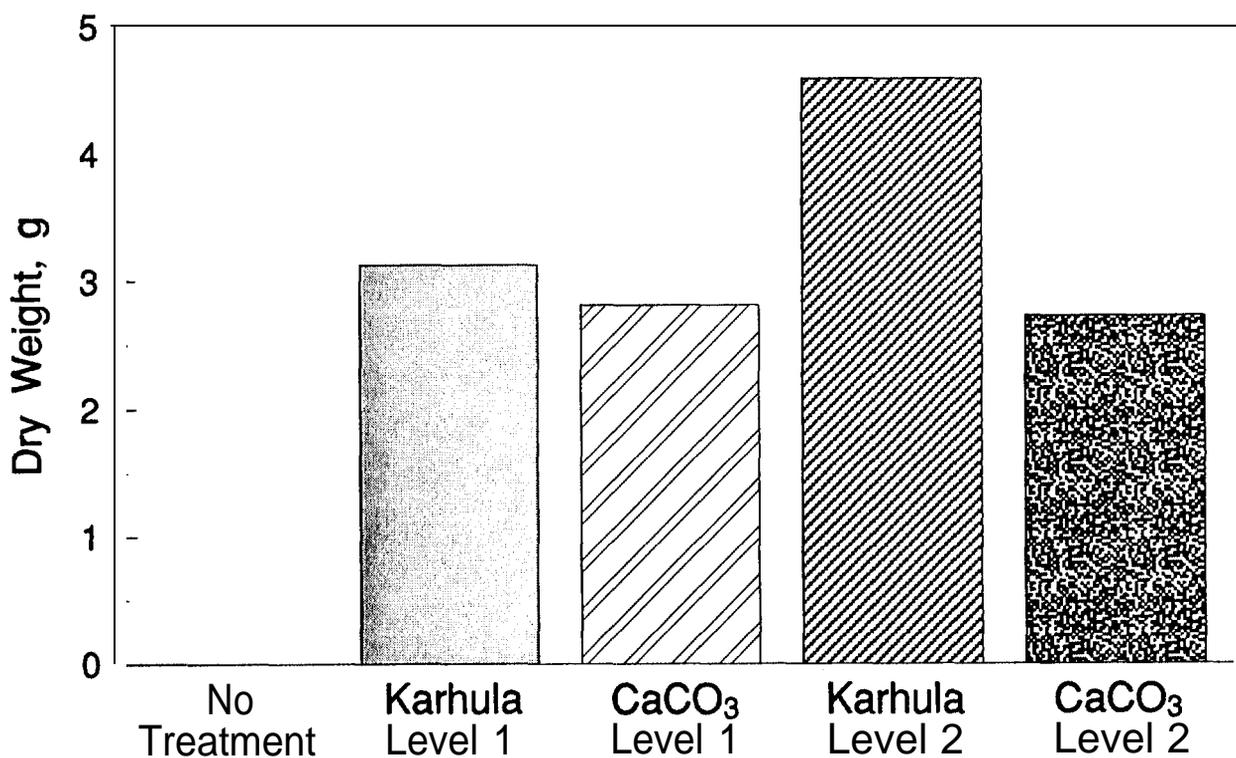
The humidity cell equilibrium study has shown the Karhula fly ash to be an effective acid spoil amendment. However, there are several differences between the ag-lime and the Karhula fly ash treated spoil materials, which may have a potential to influence the successful use of the Karhula fly ash as an agronomic soil amendment. The lower early pH levels of approximately 4 for the Karhula fly ash treated spoils could cause some problems with germination and early plant growth. In addition, the Karhula fly ash treated spoils exhibited higher EC values, especially during the early phase of the humidity cell oxidation.

**Greenhouse Studies.** Based on the results of the humidity cell equilibrium studies, a greenhouse study was conducted to compare the plant production associated with two application levels of Karhula Ca/S=1 fly ash to two levels of application of  $\text{CaCO}_3$  (ag-lime). The greenhouse study is designed to show the influence of the neutralization potential and the nutritional content of the ash on plant production.

Garrison meadow foxtail grass (*Alopecurus profensis, cult. Garrison*) was selected as the test species. Meadow foxtail grass is commonly used in the Rocky Mountain states of Wyoming and Colorado to create productive grasslands. An acidic spoil material used in the equilibrium studies was used for the greenhouse studies.

The greenhouse study was conducted under controlled conditions of light, temperature, fertilizer levels, and soil moisture requirements to maximize plant growth conditions. Fertilizer additions were based on N, P, and K levels and did not include concerns for nutrient ratios and micronutrient deficiencies.

The plant production results for the first cutting are presented in Figure 9. Photographs showing the results of the first cutting of the Meadow foxtail grass grown in acid spoil amended with ag-lime and Karhula Ca/S=1 fly ash are presented in Figures 10 and 11.



**Figure 9. Dry Weight Production of Meadow Foxtail Grass Grown on Karhula Ca/S=1 Fly Ash and Ag-Lime Amended Acidic Mine Spoil**



**Figure 10. Photograph of the Production of Meadow Foxtail Grass Grown on Ag-Lime Amended Mine Spoil**



**Figure 11. Photograph of the Production of Meadow Foxtail Grass Grown on Karhula Ca/S=1 Fly Ash Amended Mine Spoil And Spoil With No Amendment**

It is very apparent that the untreated acid spoil was unable to support any plant growth, as the seeds did not germinate. The Karhula fly ash amended spoil material resulted in yields comparable to those of the ag-lime amended spoils at the high amendment application rate (level 1) and clearly resulted in higher plant production than the ag-lime at lower amendment rates (level 2). This was somewhat unexpected, based on the higher pH and EC of the ag-lime amended spoil. These findings possibly are due to nutritional issues rather than to pH/EC conditions. These issues are being considered at the present time.

## **SUMMARY AND CONCLUSIONS**

In summary, WRI, in conjunction with the Electric Power Research Institute, Ahlstrom Pyropower and the U.S. Department of Energy, has undertaken a research and demonstration program designed to examine the market potential and the technical feasibility of ash use options for PFBC ashes. The market assessment has indicated ash markets in both the construction and the agriculture and reclamation industries.

The technical feasibility study examined the use of PFBC ash in construction-related applications, including its use as a supplemental cementing material in concrete, fills and embankments, soil stabilization, and synthetic aggregate production. Testing was also conducted to determine the technical feasibility of PFBC ash as a soil amendment for agricultural and reclamation applications.

PFBC ash does not meet the chemical requirements as a pozzolan for cement replacement. However, it does appear that potential may exist for its use in cement production as a pozzolan and/or set retardant.

PFBC ash shows relatively high strength development, low expansion and low permeability properties that make its use in fills and embankments promising.

Testing has also indicated that PFBC ash, when mixed with low amounts of lime, develops high strengths, suitable for soil stabilization applications and synthetic aggregate production. Synthetic aggregate produced from PFBC ash is capable of meeting ASTM/AASHTO specifications for many construction applications.

The residual calcium carbonate and calcium sulfate in the PFBC ash has been shown to be of value in making PFBC ash a suitable soil amendment for acidic soils. Additional testing is planned, and field demonstrations are to be conducted dependent upon the results of this testing.

In conclusion, PFBC ash should be viewed as a valuable resource and ash use options explored for this material for planned PFBC installations.

## **DISCLAIMER**

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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